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PATENT SPECIFICATION

NO DRAWINGS

982,756



982,756

Date of Application and filing Complete Specification: Dec. 13, 1963.
No. 49287/63.

Application made In United States of America (No. 246,340) on Dec. 21, 1962.
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Index at acceptance:—H1 H(2, 3C, 3E, 3F, 6B, 9)

Int. Cl.:—H 01 d

COMPLETE SPECIFICATION
Process for Sintering a Ferrite Body

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ERRATUM

SPECIFICATION No. 982,756
Amendment No. 1

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Page 4, line 8, for "coincident" read "co-
incident"

THE PATENT OFFICE
22nd September 1965

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For, in a coincident memory device, two current pulses, each of which alone is of insufficient intensity to produce switching, are applied to the device to switch the body from one of its remanent states of magnetization to the other. Where maximum squareness is not realized in the device, partial switching may occur with only one pulse, i.e. undesired signals may be produced which are difficult to distinguish from desired signals.

Procedures for producing ferrospinel ferrite bodies having a substantially square hysteresis loop characteristic are well-known. These ferrites are generally synthesized by mixing selected constituent metallic oxides in predetermined proportions, processing the mixture to a powder by standard ceramic processing methods, pressing the powder into rigid shape and, thereafter, sintering the pressed material at a high temperature. The treatment causes the constituents to react and diffuse on [Price 4s. 6d.]

from a mixture comprising trivalent ferric oxide and at least one bivalent metal oxide, including controlling said ambient so that it contains some but not more than 3% by volume of water vapor, and reacting said body in said ambient at a temperature sufficiently high to produce solid-state reactions within said body.

It has been found that the water vapor is most effective during the oxygen absorption phase of the sintering treatment. It appears to have some influence on the kinetics of the oxygen pick-up and it is most beneficial when utilized during this phase of the treatment. From what has been determined, the water vapor appears to have a catalytic effect on the ferrite formation reactions on which the final magnetic characteristics of the ferrite bodies largely depend.

The amount of water vapor in the oxidising ambient during the sintering treatment is

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COMPLETE SPECIFICATION

Process for Sintering a Ferrite Body

We, INTERNATIONAL BUSINESS MACHINES CORPORATION, a Corporation organized and existing under the laws of the State of New York in the United States of America, of

5 590 Madison Avenue, New York 22, State of New York, United States of America (assignees of ALLAN GETTO) do hereby declare the invention for which we pray that a patent may be granted to us, and the method by

10 which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for sintering a ferrite body made from a mixture comprising trivalent ferric oxide and at least one bivalent metal oxide.

15 Ferrospinel bodies are employed as magnetic memory elements and as pulse transfer elements in computers and other data processing machines. The characteristic shape of the hysteresis loop for these bodies is of particular importance, especially where the ferrospinel body is employed as a coincident current memory device which, to a large degree, depends on the ferrospinel body having a substantially square hysteresis loop characteristic. For, in a coincident memory device, two current pulses, each of which alone is of insufficient intensity to produce switching, are applied to the device to switch the body from one of its remanent states of magnetization to the other. Where maximum squareness is not realized in the device, partial switching may occur with only one pulse, i.e. undesired signals may be produced which are difficult

20 to distinguish from desired signals.

25 Procedures for producing ferrospinel ferrite bodies having a substantially square hysteresis loop characteristic are well-known. These ferrites are generally synthesized by mixing selected constituent metallic oxides in predetermined proportions, processing the mixture to a powder by standard ceramic processing methods, pressing the powder into rigid shape and, thereafter, sintering the pressed material at a high temperature. The treatment causes the constituents to react and diffuse on

[Price 4s. 6d.]

an atomic scale to form a ferrospinel crystal structure within the pressed body of material and provides the body with a square hysteresis loop characteristic.

30 In making these ferrites, it is very difficult to maintain uniformity in the magnetic characteristics between the ferrite bodies resulting from a continuous process due to the many variables which affect the process. Normally only a proportion of the resulting ferrite bodies can be used satisfactorily as memory elements. The variables which affect the processing of square loop ferrites, and the control of these variables, have therefore been the subject of much research.

35 We have discovered that water vapor, when admitted in a limited amount during the sintering treatment of ferrite bodies containing trivalent ferric oxide and at least one divalent metal oxide, increases the proportion of the resulting ferrite bodies that are useful as memory elements.

40 According to the invention, there is provided a process for sintering a ferrite body in an oxidising ambient, the ferrite body being made from a mixture comprising trivalent ferric oxide and at least one bivalent metal oxide, including controlling said ambient so that it contains some but not more than 3% by volume of water vapor, and reacting said body in said ambient at a temperature sufficiently high to produce solid-state reactions within said body.

45 It has been found that the water vapor is most effective during the oxygen absorption phase of the sintering treatment. It appears to have some influence on the kinetics of the oxygen pick-up and it is most beneficial when utilized during this phase of the treatment. From what has been determined, the water vapor appears to have a catalytic effect on the ferrite formation reactions on which the final magnetic characteristics of the ferrite bodies largely depend.

50 The amount of water vapor in the oxidising ambient during the sintering treatment is

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- critical. Where the ambient consists of air and water vapor, the magnetic characteristics of the resulting ferrite bodies are deleteriously affected with more than 3% by volume of water vapor, while more than 5% by volume has a very serious effect. It is preferred to employ at least 1/2% by volume of water vapor in the oxidising ambient, although lower amounts may be used if desired.
- Preferably the sintering includes firing and annealing steps. The firing is performed at a temperature at which the spinel phase is stable and at which crystal grain growth continues, thereby permitting the cations and the anions of the mixed constituents to diffuse and form the spinel structure. The annealing step involves a brief cooling from the firing temperature, which is usually in the range from 1100°C to 1500°C, to a temperature below the firing temperature but which is sufficiently high to maintain the oxygen absorption and chemical formation reactions. It is during the second phase of the sintering treatment—the cooling—that the utilization of the water vapor in limited amount is most effective. From what has been found, the ambient surrounding the ferrites during the firing phase is not critical, provided it is not a reducing atmosphere, but the ambient that surrounds the ferrite during the annealing step, that is cooling the ferrite to a temperature lower than the firing temperature but one which is sufficiently high to maintain oxidation and chemical formation reactions, is most critical. During the cooling step it is essential that the ambient permit oxygen absorption and, as heretofore indicated, the water vapor assists in this requirement.
- To more fully explain the present invention, the following generalized description with specific examples is given.
- Prior to undergoing the sintering treatment of the present invention, conventional ceramic processing methods are used to convert metal oxide raw materials into ferrites having desired magnetic characteristics. The procedure is to start with oxide raw materials which are substantially pure, and have as fine a particle size as are commercially obtainable. Those oxide raw materials are then mixed with a mixing medium, usually water, and milled in a steel ball mill. Although the ball mill is commonly used, other mixing devices such as colloid mills and attritors may be used. After milling, the homogenous oxide mixture is oven dried, and the resulting cake after pulverization, is presintered, which presintering consists of heat treating the oxide mixture at a temperature somewhat lower than the final
- firing temperature. All or part of the oxide mixture may be presintered for it has been shown that the presintering is helpful in controlling shrinkage in the final shape, and influence grain parameters, size and shape, and homogeneity; however the presintering step may be completely eliminated in certain manufacturing processes. After presintering, or if no presintering is used, after calcining, the oxide mixture is comminuted to a particle size that is ceramically workable, and organic binders are added to serve as a binder and particle lubricant. Conventional means such as dry presses or extruding equipment are then used to press the oxide mixture into desired shapes. The shaped metal oxide mixture is then in the final stages before it undergoes the process of the present invention.
- A specific example of a ferrite is one which comprises 40% Fe_2O_3 , 55% MnCO_3 and 5% CuO , and with this ferrite the calcining is done at a temperature from 600°C to 1000°C for approximately a time interval ranging from 30 to 180 minutes. The organic binder is 3% polyvinyl alcohol, and the lubricant is 1/4% by weight dibutyl phthalate. The pressing is done to a density between about 2.5 to 4.0 grams per cubic centimeter.
- Following conventional ceramic procedures, the Cu-Mn ferrite is fired at 1250°C for about 10 minutes (the time and temperature is a function of the composition and may vary from 1100°C to 1500°C for periods of 2 minutes to 4 hours). After the firing step, the ferrite is annealed in an ambient containing air and 1/2% to 3% by volume of water vapor. The annealing step entails cooling the ferrite to a temperature of about 900°C which for the Cu-Mn ferrite requires about 10 to 15 minutes. As previously indicated the ambient about the ferrite during the firing step need not include the air-water vapor mixture, but in many sintering plants presently available, it may be more economical to include the water vapor rather than to exclude it.
- As heretofore stated, the upper percentage of water vapor utilized in the ambient is most critical in that the square loop characteristics seriously deteriorate if more than 5% water vapor is utilized. The beneficial effects of the water vapor are illustrated by the data in the table below for an air-water vapor ambient. In the Table uV_1 is the undisturbed one signal, rV_1 the read disturber one signal, wV_2 the write disturbed zero signal, T_s the switching time, and rV_1/wV_2 , the one to zero ratio which is a standard definition for squareness in the art:

TABLE

Comp.	Water Temp. °C.	% H ₂ O by vol.	Stagnant Air			Annealing Temp. °C.	Magnetic Parameters		
			Firing Temp. (°C.)	Cycle Time (min.)	uV ₁ (mv)		rV ₁ (mv)	wV ₂ (mv)	T ₃ μsec.
1	—	—	1200	8	920	40	38	9.2	1.00
2	25	3.0	1200	8	920	44	41.5	9.9	1.02
3	37	6.0	1200	8	920	56	22	.48	.96
4	47	10.5	1200	6-1/2	920	60	13	.54	.8
5	62	21.5	1200	6-1/2	920	56	12	.50	.75
6	82	50.0	1200	6-1/2	920	54	15	.47	—
7	100	100.0	1200	6-1/2	920	18	12	.10	—
8	62	21.5	1200	6-1/2	920	59	13	.50	.75
9	62	21.5	1170	6	900	72	31	.50	—

Reference to the Table indicates that in the ambients containing more than 5% water vapor, the one-to-zero disturbed signal ratio is drastically affected. Note that at 3% water vapor the rV_1/wV_2 is 4.5 while at 6% water vapor the ratio is 0.55. Ferrites from the latter treatment give extremely poor responses when used as concident memory devices. The situation is further aggravated as the amount of water vapor is increased in the ambient.

With $\frac{1}{2}\%$ to 3% by volume of water vapor in the oxidising ambient surrounding the ferrite during the sintering treatment, a catalytic reaction is produced which increases the yield of ferrites useful as memory elements from a continuous process treatment of the material. The exact nature of the catalytic effect of the water vapor has not been determined and various explanations may be offered to explain the effect of the water vapor. It may be that the water vapor produces surface migration of the ions and promotes the solid-state reactions which are necessary in the fabrication of square loop ferrite. Or, it may be that the water vapor facilitates nucleation, promotes surface diffusion and expands the reaction sites. Further specific examples of typical three cation and two cation ferrite systems which benefit from the present invention are:— Mn-Zn-Fe, Ni-Zn-Fe, Mg-Mn-Fe, Mn-Fe, Ni-Fe, Zn-Fe, Cu-Fe and Mg-Fe. In these systems, the firing is performed at temperatures between 1100°C to 1500°C, while the temperature to which these ferrites are annealed is necessarily dependent upon the particular ferrite composition in question, although it is generally above 600°C.

The process of the invention is defined in the appended claims. We disclaim processes in which the ferrite body is reacted in atmospheric air in which the water vapor content is not controlled.

WHAT WE CLAIM IS:—

1. A process for sintering a ferrite body in an oxidising ambient, the ferrite body being made from a mixture comprising trivalent ferric oxide and at least one bivalent metal oxide, including controlling said ambient so that it contains some but not more than 3% by volume of water vapor, and reacting said body in said ambient at a temperature sufficiently high to produce solid-state reactions within said body. 45
2. A process as claimed in claim 1 in which controlling of the ambient includes admitting to the ambient a limited amount of water vapor. 50
3. A process as claimed in claim 1 or 2, in which said ambient contains at least $\frac{1}{2}\%$ by volume of water vapor. 55
4. A process as claimed in claim 1 or 2 or 3 in which said body is fired at a temperature sufficiently high to produce solid state reactions within said body to provide the body with a spinel structure, the reacting of said body in an oxidising ambient then being carried out while the fired body is being cooled from the firing temperature. 60
5. A process as claimed in claim 4 in which the firing temperature is between 1100°C and 1500°C. 65
6. A process as claimed in any one of the preceding claims in which the oxidising ambient, apart from the water vapor, consists of air. 70
7. A process for sintering a ferrite body substantially as herein described in the examples. 75
8. A spinel ferrite body sintered by a process as claimed in any one of the preceding claims. 80

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Agent for the Applicants.

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